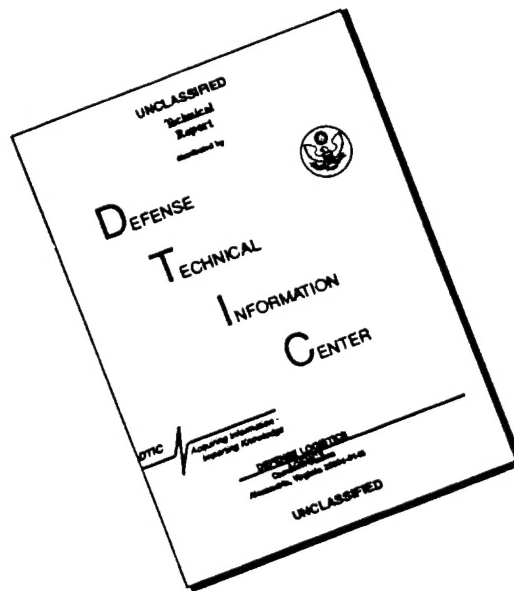


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13. ABSTRACT (Maximum 200 words) The 1996 Asilomar Conference on Polymeric Materials focused on computational design and tailoring of new polymeric materials. Current new directions were probed followed by descriptions of new scientific opportunities. An attempt was made to understand and predict structure-property-processing relationships by using the hierarchical approach to describe complex materials systems. Special emphasis were on modeling of polymers using advanced computer methods, and on the design and synthesis of new polymeric materials used on the predictions elucidated from these computational advances. This conference addressed the problems and opportunities that are arising with the emergence of an hierarchical approach to the design of new materials systems. It was organized along multidisciplinary lines in order to accommodate the perceived needs for the translation of the existing knowledge between disciplines. The most advanced polymeric systems of today were addressed. Speakers and conferees were selected from the materials sciences and engineering disciplines, the biological sciences, and various branches of chemistry and applied physics including mechanics.				
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PROCEEDINGS

NINETEENTH ASILOMAR CONFERENCE ON POLYMERIC MATERIALS

February 11-14, 1996

SPONSORED BY

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SUBMITTED BY

Eric Baer
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

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PROGRAM

Asilomar

CONFERENCE



*Nineteenth
Asilomar Conference
on Polymeric Materials*

February 11-14, 1996

Pacific Grove, CA

THE NINETEENTH ASILOMAR CONFERENCE
ON POLYMERIC MATERIALS
February 11-14, 1996

Invited Speakers

"NEW MICROLAYERED MATERIALS"

PROFESSOR ERIC BAER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OH

**"MOLECULAR DYNAMICS COMPUTER SIMULATIONS OF
POLYMER LIQUID CRYSTALS"**

PROFESSOR WITOLD BROSTOW
UNIVERSITY OF NORTH TEXAS
DENTON, TX

"MODELING OF FIBROUS PROTEINS FOR NEW BIOMATERIALS"

DR. STEPHEN FOSSEY
U.S. ARMY
NATICK, MA

**"DYNAMICS OF POLYMERIC FLUIDS - INFLUENCE OF FLOW ON
MICROSTRUCTURE"**

DR. GERALD FULLER
STANFORD UNIVERSITY
STANFORD, CA

"DESIGN OF MACROMOLECULAR MATERIALS"

PROFESSOR WILLIAM GODDARD
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CA

**"RELATIONSHIPS AMONG MOLECULAR ARCHITECTURE,
SOLID STATE STRUCTURE AND MECHANICAL PROPERTIES OF
CGCT POLYETHYLENES"**

PROFESSOR ANNE HILTNER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OH

"POLYMER COMPOSITES WITH INCREASED TOUGHNESS"

DR. ROBERT KOVAR
FOSTER MILLER, INC.
WALTHAM, MA

"DEGREES OF FREEDOM IN CELLULAR SOLIDS AND COMPOSITE MATERIALS"

PROFESSOR ROD LAKES
UNIVERSITY OF IOWA
IOWA CITY, IA

"MODEL SEMICRYSTALLINE IONOMERS"

PROFESSOR ROBERT MOORE
UNIVERSITY OF SOUTHERN MISSISSIPPI
HATTIESBURG, MS

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PROFESSOR PAUL PAINTER
PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PA

"SIMULATION OF TEMPERATURE-DEPENDENT BEHAVIOR OF POLYMERS"

PROFESSOR GREGORY RUTLEDGE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MA

"SELF ASSEMBLING MULTIFUNCTIONAL MATERIALS"

PROFESSOR SAMUEL STUPP
UNIVERSITY OF ILLINOIS
URBANA, IL

"MOLECULAR MODELS FOR POLYMER DEFORMATION AND FAILURE"

DR. YVES TERMONIA
E.I. DUPONT
WILMINGTON, DE

"DENDRITIC POLYMERS: A FOURTH NEW CLASS OF POLYMER ARCHITECTURE"

DR. DONALD TOMALIA
MICHIGAN MOLECULAR INSTITUTE
MIDLAND, MI

"DESIGN OF NEW POLYMERS FOR PHOTONICS AND ELECTRONICS"

DR. SUKANT TRIPATHY
UNIVERSITY OF MASSACHUSETTS, LOWELL
LOWELL, MA

Attendees
Nineteenth Asilomar Conference
February 11-14, 1996

Dr. Kirk Abbey
Lord Corporation
Cary, NC 27511

Prof. Eric Baer
Case Western Reserve University
Cleveland, OH 44106

Dr. Rolf Baumhake
Leiter Polymerphysik, Bayer AG
Leverkusen, GERMANY

Dr. Bill Beever
Phillips Petroleum Company
Bartlesville, OK 74004

Prof. Witold Brostow
University of North Texas
Denton, TX 76203

Dr. Larry Charbonneau
Hoechst Celanese Corporation
Summit, NJ 07901

Dr. C.P. Christenson
Dow Chemical Company
Midland, MI 48674

Dr. Steve Chum
Dow Chemical Company
Freeport, TX 77541

Prof. Michael Coleman
Pennsylvania State University
University Park, PA 16802

Dr. Mark Conner
Air Products & Chemicals, Inc.
Allentown, PA 18195

Dr. Andrew Crowson
U.S. Army Research Office
Research Triangle Park, NC 27709

Dr. A. Cunningham
ICI Polyurethanes
Everberg, BELGIUM

Dr. Ronald DeMartino
Hoechst Celanese Research Corp.
Summit, NJ 07901

Dr. Stephen Fossey
U.S. Army Natick-R&D Center
Natick, MA 01760

Prof. Gerald Fuller
Stanford University
Stanford, CA 94305

Dr. Gunilla Gillberg
Kimberly Clark Corporation
Roswell, GA 30076

Dr. John Gilmer
Eastman Chemical Company
Kingsport, TN 37662

Prof. William Goddard
California Institute of Technology
Pasadena, CA 91125

Dr. Martin Guest
Dow Chemical Company
Freeport, TX 77541

Dr. Gary Hagnauer
U.S. Army Research Laboratory
Aberdeen Proving Ground, MD 21005

Dr. Leonard Harvey
ICI Fluoropolymers
Downingtown, PA 19335

Prof. Anne Hiltner
Case Western Reserve University
Cleveland, OH 44106

Dr. George Hoffmann
E.I. DuPont Experimental Station
Wilmington, DE 19880

Dr. Claude Job
PECHINEY
Paris, FRANCE

Dr. Douglas Kiserow
U.S. Army Research Office
Research Triangle Park, NC 27709

Dr. Laura Kiefer
Hoechst Celanese Corporation
Charlotte, NC 28210

Dr. Lothar Kleiner
ALZA Corporation
Palo Alto, CA 94303

Dr. James Klug
3M Austin Center
Austin, TX 78726

Dr. Robert Kovar
Foster Miller, Inc.
Waltham, MA 02254

Dr. Jacqueline I. Kroschwitz
John Wiley & Sons, Inc.
New York, NY 10158

Prof. Rod Lakes
University of Iowa
Iowa City, IA 52242

Dr. Eric Larson
3M Center
St. Paul, MN 55144

Dr. Robert Matheson
DuPont Marshall Research Laboratory
Philadelphia, PA 19149

Dr. George Mayer
The Office of the Director of Res. & Eng.
Washington, D.C 20301

Prof. Robert Moore
University of Southern Mississippi
Hattiesburg, MS 39406

Dr. Charles Myers
Amoco Chemical Company
Naperville, IL 60067

Prof. Paul Painter
Pennsylvania State University
University Park, PA 16802

Dr. Edward Park
Gillette Company
Boston, MA 02127

Dr. Richard Parker
BFGoodrich Company
Brecksville, OH 44141

Dr. Brian Pengilly
430 Delaware Avenue
Akron, OH 44303

Prof. Roger Porter
University of Massachusetts
Amherst, MA 01002

Dr. Bill Prest
Xerox Corporation
Webster, NY 14580

Dr. Madhukar Rao
Sherwin-Williams Company
Cleveland, OH 44113

Dr. Patrick Reilly
Goodyear Tire & Rubber Company
Akron, OH 44305

Dr. James Rieke
Michigan Molecular Institute
Midland, MI 48640

Prof. Gregory Rutledge
Massachusetts Institute of Technology
Cambridge, MA 02139

Dr. David Schiraldi
Hoechst Celanese Corporation
Charlotte, NC 28210

Dr. Jerry Seitz
Dow Chemical Company
Midland, MI 48674

Dr. Richard Shuford
U.S. Army Research Laboratory
Aberdeen Proving Ground, MD 21005

Dr. Alexa Sommer
Bayer Corporation
Pittsburgh, PA 15205

Dr. David Squire
1032 Diamond Crest Court
Santa Barbara, CA 93110

Prof. Vivian Stannett
North Carolina State University
Raleigh, NC 27695

Prof. Samuel Stupp
University of Illinois
Urbana, IL 21801

Dr. Yves Termonia
E.I. DuPont Experimental Station
Wilmington, DE 19880

Dr. Donald Tomalia
Michigan Molecular Institute
Midland, MI 48640

Dr. Vasily Topolkaev
Kimberly Clark Corporation
Neenah, WI 54957

Dr. Sukant Tripathy
University of Massachusetts
Lowell, MA 01854

Dr. James Van Trump
E.I. DuPont Experimental Station
Wilmington, DE 19880

Dr. Stasis Zachariades
POLTECO Incorporated
Burlingame, CA 94011

NEW MICROLAYERED MATERIALS

by

Eric Baer

Department of Macromolecular Science and
Center for Applied Polymer Research
Case Western Reserve University
Cleveland, Ohio 44106

ABSTRACT

Numerous examples illustrate how the coextrusion of film with three or more polymeric layers is economically used to achieve a desirable mix of end-use characteristics. More recently, layer-multiplying devices permit two polymers of widely dissimilar solid state structures and properties to be combined into unique microlayer and nanolayer laminates with thousands of layers. Studies of layered polymer composites with hundreds or thousands of alternating layers have revealed some unique advantages achievable when the layers are thin enough to produce synergistic combinations of key properties of the constituent components.

The applications of microlayer extrusion technology can be separated into two broad areas that are illustrated with specific examples. In the first area, new materials with very thin layers are created that exhibit improved physical properties. The improved properties include mechanical, optical, barrier and electronic, and combinations of these properties. The second area of focus is in using the microlayer technology to generate a large specific surface area for fundamental studies of adhesion, diffusion and crystallization.

Molecular dynamics computer simulations of polymer liquid crystals

Witold Brostow

Departments of Materials Science and Physics

University of North Texas

Denton, TX 76203-5308

brostow@unt.edu

<http://voigt-i.srb.unt.edu>

Polymer liquid crystals (PLCs) are interesting for practical reasons since they provide reinforcement of flexible engineering polymers (EPs) at the molecular level - avoiding the adhesion problems typical in fiber-reinforced EPs ¹. PLCs are also interesting for fundamental reasons. Their structures are hierarchical; the importance of such structures for properties has been noted repeatedly by Baer, Hiltner and coworkers ². We are trying to move up and down in the hierarchies by considering different structural blocks in terms of homeomorphism - or otherwise - between them ³.

We are also trying to understand the behavior of PLCs by performing molecular dynamics (MD) simulations. We use the algorithm of Berendsen e.a. ⁴. We impose *large* external mechanical forces - to see what causes the failure of the material. Relaxational as well as destructive (crack propagation) phenomena are observed; some specific results will be presented.

1. W. Brostow, *Polymer* 1990, 31, 979.
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4. H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola and J.R. Haak, *J. Chem. Phys.* 1984, 81, 3684.

Modeling of Fibrous Proteins for New Biomaterials

Stephen Fossey, Science & Technology Directorate, U. S. Army
Natick RD&E Center, Natick, MA 01908-5020

Genetic production of protein polymers allows unprecedented control of polymer structure and morphology. Silks are protein polymers produced by many species of arachnids and insects. The cocoon silk of the silkworm has been used for thousands of years to produce high quality textile fibers. More recently, with the advent of the tools of biotechnology, it has become possible to use genetic means to duplicate spider silks. The silk of orb weaving spiders posses an unusual combination of elastic modulus, tensile strength and elongation to break. To gain a further understanding of these materials we have used molecular modeling to investigate the crystal forms as well as the structure and properties of the noncrystalline domains of silk-like polymers.

The crystal structure of silkworm silks have been simulated using molecular mechanics calculations with the ECEPP/2 forcefield. The results of these calculations have led us to propose a new model for the metastable silk I crystal form.

The noncrystalline domains are composed of amorphous regions and interphases between the crystalline and amorphous domains. It has been shown that the interphases can be an important factor in the properties of both PET and spider silk fibers. The interphases have been modeled as a statistical coil in a constrained geometry of defined thickness. The mechanical properties of these interphases have been calculated from an estimation of the second derivatives of the energy using the Polymer Consortium Software from Biosym/MSI. In addition to mechanical properties a number of other characteristics have been calculated for statistical arrangements of polypeptides in constrained geometries.

Dynamics of Polymeric Fluids: Influence of Flow on Microstructure

Gerald G. Fuller
Chemical Engineering
Stanford University
Stanford, CA 94305-5025

Hydrodynamic forces can induce important microstructural transitions in polymeric liquids. Examples would local, segmental orientation in polymer melts and blends, lamella re-orientation in block copolymers, enhancement of concentration fluctuations in multicomponent systems, and director orientation in polymer liquid crystals. These phenomena, in addition to producing profound affects on the rheological response of these materials, are important to processing flows. In this presentation, an overview is offered of flow-property relationships in polymeric liquids along with a detailed discussion of the following two cases:

1. Coupling of flow to concentration fluctuations in polymer liquids. The stresses resulting from the flow of polymeric fluids can induce a flux of polymer segments leading to large scale inhomogeneities, and in some cases even phase separation. The structure factor measured using light scattering offers a direct indication of this coupling and can be used to quantitatively test the predictions of microstructural models of this phenomena. Data are offered on polymer solutions, polymer blends, and solutions of living polymers (surfactant micelles).
2. Flow-induced orientation of polymer monolayers. Polymeric materials find many applications as thin films and the processing of these structures often involves flow processes. When forced to reside in two dimensions, chain-chain interactions are greatly enhanced and flows to modest to induce orientation for the three dimensional analogs can readily induce orientational transitions. Flow experiments performed on a Langmuir monolayer of a rigid rod polymer are described and the results are successfully compared against calculations using a two dimensional model of a polymer liquid crystal.

Nineteenth Asilomar Conference on Polymers
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DESIGN OF MACROMOLECULAR MATERIALS

W. A. Goddard III, Paul Miklis, Tahir Cagin
Materials and Process Simulation Center (MSC), Beckman Institute (139-74)
California Institute of Technology, Pasadena, CA 91125

We will discuss the use of atomistic simulations to predict the properties of macromolecules and materials with an emphasis on new materials related to starburst dendrimers,¹ etc.

As a specific application we will discuss the dendritic polyether macromolecules composed of 3,5-dihydroxybenzyl alcohol building blocks and carboxylate group chain ends, first reported by Frechet.² We will use this system to illustrate the strategies for predicting the structures and properties of dendrimer macromolecules. Here we followed the convergent approach used by Frechet in synthesizing these dendrimers. Thus we initiated conformational searching at the final branching point before the chain ends and continued inwards towards the core. We found the minimum energy conformations to be largely dependent on the torsional angles defined at the branching points, and thus the globular structure is well ordered. In addition, we performed dynamics simulations to predict the conformational effects of solvation and the ability of the dendrimers to solvate hydrophobic molecules.

We will include discussions on the choice of force fields for such studies. In addition we will discuss recent advances in the technology of molecular dynamics simulations (MPSim) which now allow atomistic studies of up to 1 million atoms.

1. Tomalia, D.A., Naylor, A.M. and Goddard, III W.A. *Angew. Chem. Int. Ed. Engl.***49**, 138-175 (1990)
2. Hawker, C.J., Wooley, K.L. and Frechet, J.M.J. *J. Chem. Soc., Perkin Trans. Part 1* **1993**, 1287 (1993).

Relationships among Molecular Architecture, Solid State Structure and Mechanical Properties of CGCT Polyethylenes

A. Hiltner, S. Bensason, S. Chum*, and E. Baer

Department of Macromolecular Science and
Center for Applied Polymer Research
Case Western Reserve University
Cleveland, OH 44109

and

*The Dow Chemical Company
Freeport, TX 77566

Ethylene-octene copolymers prepared by Dow's INSITE® constrained geometry catalyst technology present a broad range of solid state structures from highly crystalline, lamellar morphologies to the granular morphology of low crystallinity copolymers. As the comonomer content increases, the accompanying tensile behavior changes from necking and cold drawing typical of a semicrystalline thermoplastic to uniform drawing and high recovery characteristic of an elastomer. Although changes in morphological features and tensile properties occur gradually with increasing comonomer content, the combined body of observations from melting behavior, morphology, dynamic mechanical response, yielding and large scale deformation suggest a classification scheme with four distinct categories. Materials with densities higher than 0.93g/cc, Type IV, exhibit a lamellar morphology with a well-developed spherulitic superstructure. Type II polymers with densities between 0.93 and 0.91g/cc have thinner lamellae and smaller spherulites. Type II materials with densities between 0.91 and 0.89g/cc have a mixed morphology of small lamellae and bundled crystals, and can form very small spherulites. Type I copolymers with densities less than 0.89g/cc have no lamellae or spherulites. Fringed micellar or bundled crystals are inferred from the low degree of crystallinity, the low melting temperature, and the granular, non-lamellar morphology.

The elastomeric deformation behavior of Type I ethylene-octene copolymers was examined in uniaxial tension as a function of temperature. A physical network picture is proposed for these elastomers, with bundle-like crystals forming junctions of large functionality. The modulus obtained by simple rubber theory is consistent with this model. However simple rubber theory, and also the Mooney-Rivlin approach, are largely inadequate for describing the shape of the stress-strain relationship. The entire range of deformation is described by the sliplink theory.

Polymer Composites With Increased Toughness

Robert F. Kovar
Foster-Miller, Inc.
195 Bear Hill Road
Waltham, MA 02154-1196

As a result of their favorable strength-to-weight characteristics, fiber-reinforced composite materials are frequently considered as prime candidates for the fabrication of advanced aerospace structures where reduced weight and high performance is of critical importance. However, the pronounced susceptibility of composites to undetectable damage resulting from low velocity, high mass impact has seriously limited their application as primary structures. Hidden impact damage manifests itself as severe reduction in composite residual tensile and compressive strength following single event impacts with low mass, low velocity projectiles. Development of effective methods for toughening composites against the threat of impact damage will greatly facilitate the application of these materials as primary structures on advanced aircraft and spacecraft.

The impact-resistance and damage tolerance of advanced fiber-reinforced composites has been reported to be significantly improved by the application of a number of different toughening mechanisms. Successful methods for toughening composites have included the use of inherently tough matrix polymers, such as thermoplastic resins, the addition of functional, elastomeric polymers that dissolve in reactive thermoset monomers but then precipitate out as microscopic, spherical domains that chemically bond to the resin during cure, the application of thin, elastomeric coatings to fibers prior to consolidation within the composite and interleaving, the incorporation of thin, discrete layers of tough, ductile resin at lamina interfaces. The reported effectiveness of each of these methods toward increasing the toughness of fiber-reinforced composites will be discussed. The results of recent experiments involving the use of thermoplastic film interleaves in advanced thermoset and thermoplastic composites will also be presented.

Degrees of freedom in cellular solids and composite materials

Rod Lakes
University of Iowa
Department of Biomedical Engineering
Department of Mechanical Engineering
Center for Laser Science and Engineering
Iowa City, IA 52242

The question of how much freedom is to be incorporated in an elasticity theory must ultimately be decided by experiment. However, during the development of the theory of elasticity, it was by no means obvious how much freedom was necessary to describe materials. For example, the early uniconstant theory of Navier is based upon the assumption that forces act along the lines joining pairs of atoms and are proportional to changes in distance between them. This theory entails a Poisson's ratio of $1/4$, for all materials. Navier, Cauchy, Poisson, and Lamé supported this theory. Experimental measurements (about a century ago) of Poisson's ratio of about $1/3$ in common materials led to the replacement of uniconstant elasticity by the more general classical elasticity, following the continuum view of Green, which allows Poisson's ratios between -1 and $1/2$.

Recently, cellular solids have been developed which exhibit a controlled negative Poisson's ratio as small as -0.8 . Deformation mechanisms in these materials include relative rotation of micro-elements, and non-affine micro-deformation. Cellular solids with a negative Poisson's ratio exhibit superior resilience and toughness as a result of the unfolding of the cells.

Viscoelastic behavior is another form of freedom. Composite micro-structures are studied, which give rise to high stiffness combined with high viscoelastic loss. We demonstrate that such properties are most easily achieved if the stiff phase is as stiff as possible. Incorporation of a small amount of damping in the stiff phase has little effect on the composite damping. InSn alloy is characterized isothermally over 11 decades of time and frequency as a high-loss phase. Experimental results are presented for laminates consisting tungsten and of InSn alloy. The combination of stiffness and loss (the product $E \tan \delta$) exceeds that of well-known materials.

Additional freedom is possible in solids: the idea of a couple stress can be traced to Voigt in the late 1800's during the formative period of the theory of elasticity, and it was developed further by the Cosserats in 1909. In Cosserat elasticity there are characteristic lengths as additional engineering elastic constants. Recent experimental work discloses a variety of cellular and fibrous materials to exhibit such freedom, and the characteristic lengths have been measured. Holographic studies show that strain can spill over into regions which are classically forbidden. An additional degree of freedom is in structural hierarchy.

Hierarchical solids are solids in which structural elements themselves have structure. We examine several examples of natural structural hierarchy, and explore several ways in which hierarchical structure can be used to create materials with extremal material properties such as high strength, or unusual material properties, such as a negative Poisson's ratio.

Model Semicrystalline Ionomers

Robert B. Moore

Department of Polymer Science, University of Southern Mississippi

Post Office Box 10076, Hattiesburg, Mississippi 39406-0076

ABSTRACT

Syndiotactic polystyrene was lightly sulfonated to yield a new model semicrystalline ionomer. The effect of alkali metal counterion type on the crystallization kinetics of sulfonated syndiotactic polystyrene with ion contents of 1.4 mol % was investigated. For crystallization temperatures less than 180°C, the rate of crystallization was independent of counterion type. In contrast, for temperatures greater than 180°C, the rate of crystallization increased with increasing counterion size. Since the glass transition and melting temperatures were found to be constant for all counterion types, the variations in crystallization behavior were attributed to differences in chain mobility within the dynamic network of electrostatic crosslinks. At low temperatures, the rate of ion-hopping is slow for all of the counterion-forms relative to the rate of crystallization, and thus crystal growth occurred in the presence of kinetically-stable crosslinks. At high temperatures, chain diffusion is controlled by the ion-hopping process, and the kinetics of crystallization become influenced by the strengths of ionic interactions. Between 180 and 215 °C, the rate of crystallization was found to be inversely proportional to the ionic radii of the counterions. As the activation energy for ion-hopping increased with decreasing counterion size, longer periods of time were required to achieve the same degree of crystallinity.

MODELING THE PHASE BEHAVIOR OF HYDROGEN BONDED POLYMER BLENDS

Paul C. Painter and Michael M. Coleman

Polymers Program
Penn State University
University Park, PA 16802

Over the last ten years or so work in our laboratory has been largely focused upon the problem of hydrogen bonding in polymer mixtures of various types. We have developed infrared methodologies for determining parameters that describe the stoichiometry of hydrogen bonding (i.e., the number of each type of hydrogen bond present) and we have also developed a model that uses these parameters to calculate their contribution to the free energy of mixing. By assuming that non-specific interactions can be handled by solubility parameters, calculated from a set of carefully chosen group contributions (constructed so as to exclude as far as possible, association effects), we have been able to calculate phase behavior and compare our predictions to experiment for a wide range of homopolymer and copolymer systems.

In the model we have developed we write the number of configurations available to a hydrogen bonded system as:

$$\Omega = \Omega_F \Omega_H$$

where Ω_F is the number of configurations available to the non-hydrogen bonded chains, which we describe using the Flory approximation. The Ω_H term imposes the constraints due to the hydrogen bonding and requires in its calculation the probability that h-1 segments are adjacent to a chosen segment, such that they can be linked to form a hydrogen bonded chain. We originally assumed that this probability is given by Φ_B^{h-1} , where Φ_B is the volume fraction of segments of type B (we always use the subscript B to designate those segments that self-associate in the form of chains). Recent experimental and theoretical work suggests that this needs to be modified. Essentially, following de Gennes we note that in a volume defined by the radius of gyration of a chosen polymer chain, there is an enhancement of same chain relative to inter-chain contacts. There will therefore be more BB and AA contacts in mixtures of homopolymer chains of type A and type B than in low molecular weight analogues (and random AB copolymers) because of chain connectivity. This effect naturally depends upon the degree of polymerization, N, and simulations by Kumar (to be published) indicate that for $N \geq 100$ the fraction of intra-chain contacts is very significant. There are a number of important consequences of this effect that are quite general and lead to modifications of the Flory-Huggins equation for both solutions and blends. These results will be discussed.

Simulation of Temperature-Dependent Behavior of Polymers

Gregory C. Rutledge
J.R. Mares Associate Professor
Department of Chemical Engineering
M.I.T., Cambridge, MA

Chain connectivity and conformational behavior are responsible for many of the unique properties of polymers. The properties of solid polymers in particular reflect both the conformation and packing habits of the constituent chains, which in turn depend in a complicated manner on chemical architecture. This is especially true in ordered phases, i.e., crystals and liquid crystals, where the regularity of structure amplifies the influence of even small dissimilarities. Molecular modeling offers an objective approach to studying these complex interactions rigorously and quantitatively. Our focus lies in the orientation-dependent and temperature-dependent properties of polymers, which are subject to exploitation through careful processing or choice of temperature of application. In particular, valuable insight may be gained into the very different physics that arise from small changes in chemistry in the crystalline phases of several common polymers. In addition to detailed description of well-known thermomechanical behaviors, molecular simulations can offer consistent interpretations of many electrical properties as well, as is illustrated with poly(vinylidene fluoride). Besides equilibrium behavior, long time relaxation behavior of particular interest in polymers is amenable to atomistic description through appropriate combination of molecular scale characterization and continuum kinetic theory. An analysis of the alpha relaxation in alpha-phase PVDF is presented as an illustrative example. Self-consistent estimation of many properties which are difficult or impossible to measure experimentally, under conditions appropriate to their use, represents an essential step towards rational engineering and design of polymeric materials.

Self Assembling Multifunctional Materials

S. I. Stupp

Departments of Materials Science and Engineering
and Chemistry
Beckman Institute for Advanced Science and Technology
Materials Research Laboratory
University of Illinois at Urbana-Champaign

The use of molecular self assembly to create future materials that integrate various functions is in very early stages of development. From a technological standpoint, an ideal role for self assembly would be to drive the bulk self organization of molecules into functional "macroscopic" structures, without requiring multistep procedures, complex processing, or specific substrates. Such structures could integrate in interesting ways photonic, electronic, adhesive, structural, or energy transduction properties. This lecture will describe work aimed at the exploration of such systems, including the self assembly of layered structures composed of two-dimensional polymers, and a recently discovered system in which supermolecular aggregates stack to form highly functional thin films. The two-dimensional assemblies to be discussed are formed by aggregation of rod-like monomers that can react to form polydiacetylene backbones and hydrogen bonded networks as well. The materials obtained from these self assembling molecules are thermochromic, extremely stable when irradiated with laser beams, and also exhibit third order nonlinearities. A second system to be discussed containing discrete supermolecular aggregates forms films spontaneously with completely different opposite surfaces (hydrophobic and hydrophilic) as a result of polar stacking of its constituent nanostructures. Polar stacking also results in second order nonlinear optical properties and remarkably strong adhesion of the self assembled films to substrates. The lecture will close with a discussion of beginning efforts in the use of genetic algorithms to aid in the discovery of self assembled multifunctional materials.

Molecular Models for Polymer Deformation and Failure

Yves Termonia
Central Research and Development
Experimental Station
E.I. du Pont de Nemours, Inc.
Wilmington, DE 19880-0356

The presentation will review our molecular modeling studies of the factors controlling the deformation behavior of polymeric fibers and composites. The models are based on a lattice representation and they explicitly take into account the roles of chain extension, chain slippage through entanglements, primary and secondary bond breaking during failure, etc. The molecular weight and its distribution are easily accounted for by breaking a certain number of bonds or chain strands between lattice sites prior to deformation. These lattice networks are then strained and a set of thermally activated processes allows for chains to slip through entanglements and/or bonds to break at maximum extension. These processes are simulated by a Monte-Carlo approach using Eyring's chemical activation rate theory. At regular time intervals, the lattice sites are relaxed towards mechanical equilibrium by a series of fast computer algorithms which steadily reduce the net residual forces acting on those sites.

The first part of the presentation deals with the factors controlling the drawability and orientation of flexible macromolecules for the development of high strength fibers. The study clearly reveals the importance of molecular weight, entanglement density, as well as temperature and rate of drawing. The second part focuses on application to the deformation behavior of fiber-reinforced composites. The roles of fiber aspect ratio, modulus and orientation within the composite are studied. Our model results are compared with predictions from other theories and available experimental data.






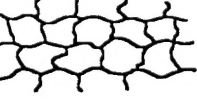
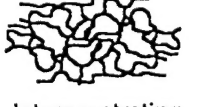
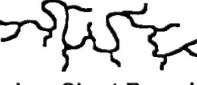
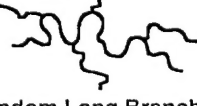
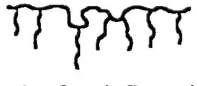

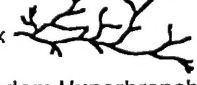
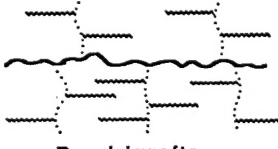
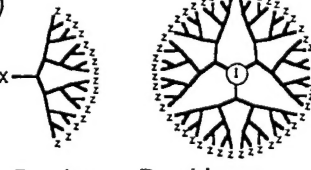
DENDRITIC POLYMERS: A FOURTH NEW MAJOR CLASS OF POLYMER ARCHITECTURE

Donald A. Tomalia

Michigan Molecular Institute
1910 W. St. Andrews Road
Midland, Michigan 48640

This new architectural class of macromolecules has received substantial attention during this past decade. Three sub-classes of this architecture which include (a) random hyperbranched (i.e., one-pot AB_x polymerizations), (b) dendrigrafts (i.e., CombburstTM polymers) and (c) regular dendrons/dendrimers (i.e., Starburst[®] dendrimers) have now been synthesized, characterized and well defined in our Laboratory. It is very clear that polymer architecture plays a critical role in defining physical properties, performance characteristics and hence commercial applications. This paper will overview these activities and focus on certain unique properties and applications that have emerged for this novel architecture.

Major Macromolecular Architectures

I	II	III	IV
Linear	Cross-Linked	Branched	Dendritic
 Flexible Coil  Rigid Rod  Cyclic (Closed Linear)  Polyrotaxane	 Lightly Cross-Linked  Densely Cross-Linked  Interpenetrating Networks	 Random Short Branches  Random Long Branches  Regular Comb-Branched  Regular Star-Branched	(a)  Random Hyperbranched (b)  Dendrigrafts (Combburst [®]) (c)  Dendrons Dendrimers (Starburst [®])
1930's -	1940's -	1960's -	1980's -

DESIGN OF NEW POLYMERS FOR PHOTONICS AND ELECTRONICS

S. K. TRIPATHY*, D. Y. KIM*, X. L. JIANG**, L. Li**, AND J. KUMAR**

University of Massachusetts Lowell, Center for Advanced Materials, Department of Chemistry* and Physics**, One University Avenue, Lowell, MA 01854

Abstract

Azo dye based polymeric systems have been extensively explored for potential applications in photonics technologies such as liquid crystal displays, nonlinear optical devices, and optical data storage media. A series of polymers with azo dye based NLO chromophores incorporated into the structure has been processed optically to fabricate holographic elements. Trans-cis-trans photoisomerization driven reorientation and macromolecular motion lead to the formation of surface relief gratings with large amplitude upon exposure to an interference pattern of visible laser beams. The amplitude of the surface modulation in a typical case was more than 1000 Å. The surface relief structures have been studied by an atomic force microscope. The gratings were very stable when kept below the glass transition temperature (T_g) of the polymers. The gratings could be erased by heating the polymer above T_g . Multiple patterns could also be written on the same film. These significant amplitude of the surface gratings due to migration of polymer chains could be observed with polymers with photoisomerizable chromophores such as azobenzene groups. We have found that photoinduced orientation of the azobenzene groups occurred first, followed by a mass diffusion process whose origin and driving force are not well understood at the present time. It has also been found that polarization states of the writing beams significantly influenced the grating formation process. When the polymer films were exposed to p-polarized beams, significantly larger diffraction efficiencies were observed compared with the film exposed to s-polarized beams. These results indicate that the grating formation process is not simply a thermal process but a complicated function of the polarization state of the writing beams. Since the amplitude of the surface variation is large (>1000 Å) and the surface relief gratings can be conveniently recorded on the polymer films, such polymers have significant potential applications for various optical devices and optical elements. Design principles of novel chromic materials will be elaborated for new photonic applications.